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Studies on Sulfenamides. XI.[1] Electron Spin Resonance Spectra of Radical Cations Electrochemically Generated from *N,N*-Disubstituted 2-Nitrobenzenesulfenamides

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The paramagnetic species formed by *in situ* electrochemical oxidation of *N*-(2-nitrophenylthio)dibenzylamine (**1**) and three *N*-methyl-4′-substituted 2-nitrobenzenesulfenanilides (4′-CH_3 (**2**), 4′-$C(CH_3)_3$ (**3**), 4′-$COOC_2H_5$ (**4**)) have been identified as the radical cations derived from the parent sulfenamides by one-electron transfer. On the other hand, the radicals generated from three 4′-unsubstituted *N*-alkyl-2-nitrobenzenesulfenanilides (N–CH_3 (**5**), N–C_2H_5 (**6**), N–$CH_2C_6H_5$ (**7**)) have been identified as the radical cations of *N,N*-dialkyl-diphenoquinone-diimines formed by dimerization of the sulfenanilide radical cations and further oxidation of the dimers. From the voltammetric data, it is proposed that the dimerization takes place before the cleavage of the S–N bond in the sulfenanilide radical cations.

Keywords——electron spin resonance; cation radical; sulfenamide; anodic oxidation; *in situ* electrolysis; sulfenamide radical cation; cyclic voltammetry; electrochemical generation; diphenoquinone-diimine radical cation; *N*-alkylsulfenanilide

Sulfenamides are important intermediates in organic synthesis and have been proven useful in investigations of lone pair interactions (α effect), bond polarization effects, and (p–d) π conjugation. Sulfenamides are used as sulfenyl-transfer reagents in the synthesis of sulfides, disulfides, trisulfides, and sulfenate esters.[2a] Interactions between the lone pairs of electrons on sulfur and nitrogen may destabilize the S–N bond and increase the nucleophilicity of the sulfenamide nitrogen, which appears to be the factor primarily determining the chemistry of sulfenamides.[2b] Industrial applications of sulfenamide derivatives include use as accelerators in rubber vulcanization, pesticides and fungicides, radioprotective agents, and in polymerization reactions.[2c]

In the previous papers,[1] we reported cyclic voltammetry and anodic oxidation of 2-nitrobenzenesulfenamides derived from secondary amines. The first step in the anodic oxidation of the sulfenamides in acetonitrile was shown to be a quasi-reversible one-electron transfer to form the sulfenamide radical cations. The formation of the radical cations were confirmed by electron spin resonance (ESR) spectroscopy. The observed non-equivalence of two N-methylene groups indicated restricted rotation around the S–N bond and the three-electron π-bonded geometry. As to the radical cations derived from six-membered alicyclic sulfenamides, the ring inversion was apparently conformationally frozen on the ESR time scale at 25 °C. The stabilities of the radical cations were also discussed.

Detection of active intermediates is a prerequisite for the elucidation of reaction mechanisms, especially when the reaction gives complex products. In our studies on the anodic oxidation of *N,N*-disubstituted sulfenamides many unexpected products were obtained. In order to clarify the mechanism of the oxidation of the sulfenamides, we studied the ESR spectra of radicals electrochemically generated from *N*-(2-nitrophenylthio)dibenzylamine (**1**) and six *N*-alkyl-2-nitrobenzenesulfenanilides in acetonitrile. Although the ESR

spectra of *N*-thioaminyl radicals have been studied extensively by many workers,[3] relatively few papers have appeared on the ESR spectra of *N*,*N*-disubstituted sulfenamide radical cations, and the chemical reactivities of the radical cations are almost unknown.[4] Since *N*,*N*-disubstituted sulfenamide radical cations are expected to be fairly stable even at ambient temperature, analysis of the ESR spectra of the radicals should afford unambiguous evidence for the structure of the radicals and facilitate the elucidation of the reaction mechanisms. Cyclic voltammetry of the sulfenamides was also studied in acetonitrile in order to obtain information on the mechanism of anodic oxidation of the sulfenamides.

Results and Discussion

Cyclic Voltammetry

Voltammetric data on **1** and *N*-alkyl-2-nitrobenzenesulfenanilides (N–CH_3, 4′-CH_3 (**2**); N–CH_3, 4′-$C(CH_3)_3$ (**3**); N–CH_3, 4′-$COOC_2H_5$ (**4**); N–CH_3 (**5**); N–C_2H_5 (**6**); N–$CH_2C_6H_5$ (**7**)) in acetonitrile containing 0.1 M $NaClO_4$ are summarized in Table I. Typical cyclic voltammograms are shown in Fig. 1. The voltammetric behavior of the sulfenamides can be classified into two groups. One is constituted of **1** and 4′-substituted *N*-methylbenzenesulfenanilides (**2**, **3**, and **4**), which show quasi-reversible anodic peaks. The other is constituted of 4′-unsubstituted *N*-alkyl-2-nitrobenzenesulfenanilides (**5**, **6**, and **7**), which show irreversible anodic peaks whose peak heights are nearly twice those of the former sulfenamides.

Radical Cations of Sulfenamides Generated by Electrochemical Oxidation

In situ electrolysis of **1** in acetonitrile at −20 °C gave a well resolved ESR spectrum as shown in Fig. 2. The radical was fairly unstable at room temperature. When the electrolytic

TABLE I. Results of Cyclic Voltammetry of the Sulfenamides in Acetonitrile

Compd. No.	Sulfenamide[a]	E_p[b]	$i_{pa} \cdot C^{-1} \cdot v^{-1/2}$[c]	i_{pc}/i_{pa}[d]
1	R-S-N($CH_2C_6H_5$)$_2$	1.31	2.3	0.5
2	R-S-N(CH_3)C_6H_4-4′-CH_3	1.15	2.6	0.7
3	R-S-N(CH_3)C_6H_4-4′-$C(CH_3)_3$	1.15	2.2	0.8
4	R-S-N(CH_3)C_6H_4-4′-$COOC_2H_5$	1.43	2.6	0.4
5	R-S-N(CH_3)C_6H_5	1.17	5.1	0
6	R-S-N(C_2H_5)C_6H_5	1.16	4.9	0
7	R-S-N($CH_2C_6H_5$)C_6H_5	1.25	4.6	0

a) The concentration of substrate was 2 mM; R = 2-nitrophenyl. *b*) Anodic peak potential in V *vs.* saturated calomel electrode (S.C.E.), sweep rate 50 mV/s. *c*) i_{pa}, anodic peak current in μA; C, concentration in mM; *v*, sweep rate in mV/s. *d*) i_{pc}, peak current of the cathodic counterpart obtained by reversal of the scan.

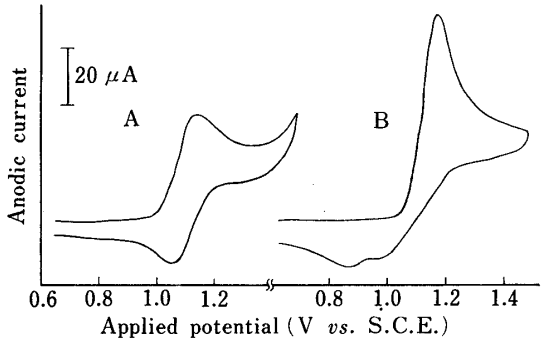

Fig. 1. Cyclic Voltammograms of the Sulfenanilides **2** (A) and **5** (B)

The concentrations of substrates were 2 mM in acetonitrile containing 0.1 M $NaClO_4$; glassy carbon anode; voltage sweep rate 50 mV/s; 25 °C.

TABLE II. ESR Parameters of the Cation Radicals Electrochemically Generated from *N*-Alkyl-2-nitrobenzenesulfenamides[a)]

Parent compound	Temp. (°C)	*g*-Value	Hyperfine coupling constants (G)[b)]	k_{obs} (min^{-1})[c)]
1	−20	2.0063	13.4 (1N), 10.2 (2H), 9.9 (2H), 1.0 (2H), 0.9 (1H)	21
2	25	2.0031	9.7 (1N), 9.4 (6H), 4.5 (2H), 1.0 (2H)	2.9
3	25	2.0030	9.5 (1N), 9.2 (3H), 4.4 (2H), 1.0 (2H)	2.3
4	−40	2.0042	10.2 (1N), 9.6 (3H), 4.15 (2H), 1.0 (2H)	11[d)]
5	25	2.0025	3.75 (2N), 3.75 (6H), 2.5 (4H), 1.25 (4H)	0.10
6	25	2.0026	3.85 (2N), 2.55 (4H), 2.5 (2H), 1.85 (2H), 1.35 (4H)	0.13
7	25	2.0027	3.7 (2N), 2.5 (6H), 1.95 (2H), 1.25 (4H)	0.59
8	25	2.0025	3.75 (2N), 3.75 (6H)	0.034
9	25	2.0025	3.9 (2N), 2.45 (2H), 1.95 (2H)	0.11

a) The radicals were generated by *in situ* electrolysis in acetonitrile containing 0.1 M $NaClO_4$. *b*) Estimated error, ±0.1 G. *c*) First-order rate constant for the decomposition of the radicals at 25 °C unless otherwise stated. *d*) At 0 °C.

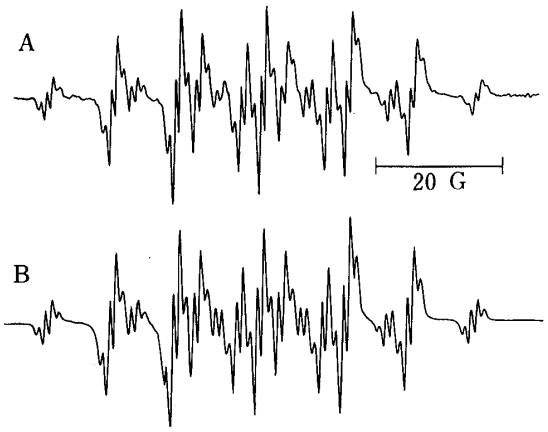

Fig. 2. ESR Spectrum of an *in Situ* Electrolyzed Solution of the Sulfenamide **1** (10 mM) in Acetonitrile (0.1 M $NaClO_4$) at −20 °C (A) and Its Computer Simulation (B)

In all spectra the magnetic field increases from left to right. Instrumental settings: power 1 mW; modulation amplitude 0.2 G; scan rate 25 G/min; gain 1 × 1000. Computer simulation was performed by using the coupling constants given in Table II and a line width of 1.0 G (Lorentzian line shape).

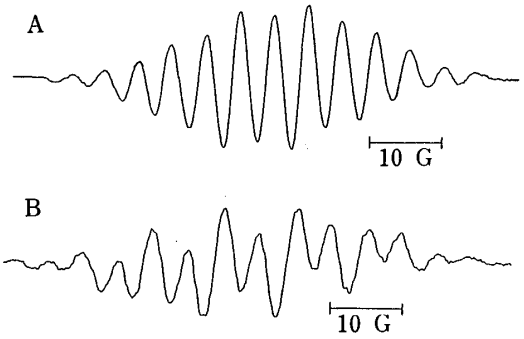

Fig. 3. ESR Spectra of *in Situ* Electrolyzed Solutions of the Sulfenanilides **3** (10 mM) at 25 °C (A) and **4** (10 mM) at −40 °C

Instrumental settings: power 1 mW; modulation amplitude A 0.8 G, B 0.63 G; scan rate A 50 G/min, B 25 G/min; gain A 5 × 100, B, 1 × 1000.

current was turned off, the ESR signal intensity decayed with first-order kinetics. The apparent first-order rate constants obtained at 25 °C are listed in Table II. The spectrum was reasonably well simulated by the ESR parameters listed in Table II. The *g*-factor and nitrogen hyperfine splitting constant (hfsc) are similar to those reported for the radical cations of alicyclic sulfenamides[1)] and *N*,*N*-dialkylmethanesulfenamides.[4a)] However, the difference in the values of hfsc's between the two methylene groups was rather small compared with that of *N*,*N*-diethylmethanesulfenamide.

Electrolysis of **2** and **3** gave fairly stable radicals at 25 °C. The ESR parameters required to match the experimental spectra by computer simulation are summarized in Table II. Although the values of *g*-factors are fairly small compared with that of $\mathbf{1}^{\cdot+}$, the values of hfsc's are consistent with those expected for radical cations of sulfenamides. Since cyclic voltammograms of **2** and **3** indicate that the first step in the anodic oxidation of **2** and **3** is a quasi-reversible one-electron transfer, the radicals detected by ESR can be assigned to the radical

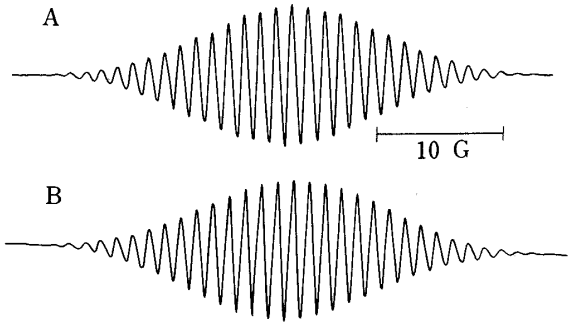

Fig. 4. ESR Spectrum of an *in Situ* Electrolyzed Solution of the Sulfenanilide **5** (10 mM) at 25 °C (A) and Its Computer Simulation (B)

Instrumental settings: power 1 mW; modulation amplitude 0.2 G; scan rate 12.5 G/min; gain 5 × 100.

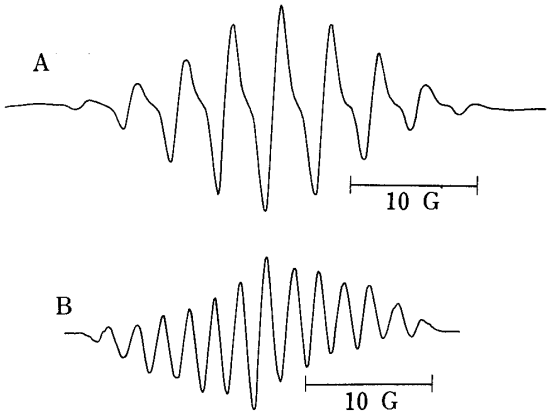

Fig. 5. ESR Spectra of *in Situ* Electrolyzed Solutions of the Deuterated Sulfenanilides **8** (10 mM) and **9** (2 mM) at 25 °C

Instrumental settings: power A 0.2 mW; B 1 mW; modulation amplitude A 0.32 G, B 0.4 G; scan rate 25 G/min; gain A 2 × 100, B 5 × 100.

cations of **2** and **3**. As can be seen from the i_{pc}/i_{pa} value of **4**, the radical cation of **4** is too labile to be detected by ESR at ambient temperature. Therefore, the first-order rate constant for the decay of the radical was measured at 0 °C. The ESR spectrum obtained by *in situ* electrolysis of **4** at −40 °C (Fig. 3) was reasonably well simulated by the ESR parameters listed in Table II, which are similar to those of $2^{+\cdot}$ and $3^{+\cdot}$.

Radicals Generated from 4′-Unsubstituted *N*-Alkyl-2-nitrobenzenesulfenanilides

Electrolysis of **5**, **6**, and **7** gave very stable radicals at room temperature (Fig. 4). The ESR spectra could not be simulated by ESR parameters expected for the radical cations of the sulfenamides. Since cyclic voltammograms of **5**, **6**, and **7** gave no cathodic counterpart of the first anodic wave on reversal of the scan, it is suggested that the radicals detected by ESR are not the radical cations of **5**, **6**, and **7** but secondary radicals which are formed by the decomposition of the radical cations followed by oxidation.

In order to clarify the structures of these radicals, *N*-methyl-2-nitrobenzenesulfenanilide-2′,3′,4′,5′,6′-d_5 (**8**) and *N*-ethyl-2-nitrobenzenesulfenanilide-2′,3′,4′,5′,6′-d_5 (**9**) were synthesized. *In situ* electrolysis of **8** and **9** gave simple ESR spectra as shown in Fig. 5, whose ESR parameters were unambiguously determined (listed in Table II).

The ESR spectra of the radicals generated from **5**, **6**, and **7** were also well simulated with the hfsc's listed in Table II which were deduced from those of the deuterated compounds. Hyperfine couplings with two nitrogens and two methyl groups or two methylene groups indicate that the radicals were formed by the dimerization of the parent sulfenanilides. Two types of dimerized radicals can be considered. One is *N*,*N*′-dialkylhydrazine radical cations, whose nitrogen hfsc's were reported to be around 11 G.[5] The nitrogen hfsc's of the radicals derived from **5**, **6**, and **7** are 3.7—3.9 G. Therefore, it is concluded that the radicals are not hydrazine radical cations. The other is *N*,*N*′-dialkyl-diphenoquinone-diimine radical cations which are formed through dimerization at the 4′-position followed by oxidation. The experimental results that **2**, **3**, and **4**, which have a substituent at the 4′-position, gave no dimerized radicals but gave the radical cations of sulfenanilides substantiate the occurrence of this type of dimerization.

Since the radicals generated from **5**, **6**, and **7** are very stable even at room temperature, they are considered to have highly conjugated structures and no 2-nitrophenylthio group. The similarity of the hfsc's of the radicals derived from **5**, **6**, and **7** to those of the *N*,*N*,*N*′,*N*′-tetramethylbenzidine radical cation also supports this conclusion.[6] From these results the

radicals generated from **5**, **6**, and **7** were identified as the radical cations of *N*,*N*′-dialkyl-diphenoquinone-diimines (di-CH_3 ($\mathbf{10}^{+\cdot}$), di-C_2H_5 ($\mathbf{11}^{+\cdot}$), di-$CH_2C_6H_5$ ($\mathbf{12}^{+\cdot}$)).

Although the six protons in the two methyl groups of $\mathbf{10}^{+\cdot}$ have the same hfsc, the four protons in the methylene groups of $\mathbf{11}^{+\cdot}$ and $\mathbf{12}^{+\cdot}$ are not equivalent but are split into two groups, both of which contains two protons. Since the two nitrogen atoms in $\mathbf{11}^{+\cdot}$ and $\mathbf{12}^{+\cdot}$ are equivalent, the radicals are considered to have a plane of symmetry. Thus, the two protons in one methylene group are considered to have different hfsc's. This suggests that rotations around the C–N bonds are slow on the ESR time scale.

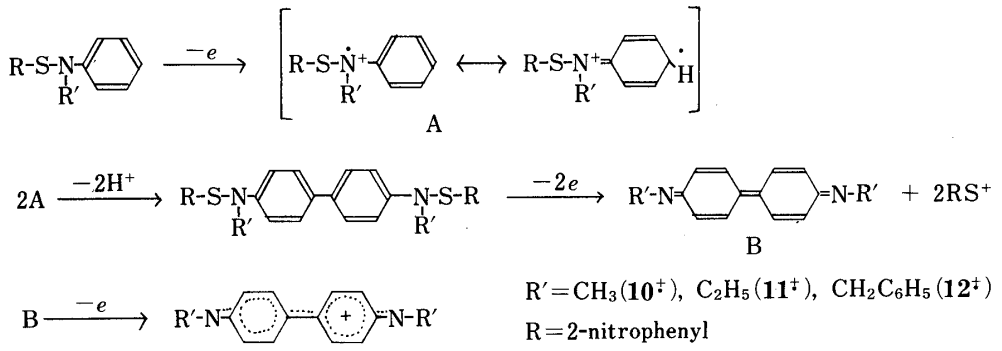

Chart 1

The following schemes are proposed for the formation of the radical cations of *N*,*N*′-dialkyl-diphenoquinone-diimines. Since all the radical cations of the 4′-substituted sulfenanilides are much more stable than those of the 4′-unsubstituted sulfenanilides, regardless of electronic effect of the substituents, the difference in the easiness of S–N bond fission between the 4′-substituted and 4′-unsubstituted sulfenanilides is supposed to be rather small. Therefore, the dimerization of the radical cations of the 4′-unsubstituted sulfenanilides is considered to take place before the S–N bond fission. Further oxidation of the dimers takes place immediately, which brings about an increase in the peak height of the first anodic waves. If two 2-nitrophenylthio groups were retained in the radicals detected by ESR, the expected coulometric *n*-value is calculated to be 1.5. Since the value of $i_{pa}C^{-1}v^{-1/2}$ of **5** is about twice that of **2**, the 2-nitrophenylthio groups should be lost immediately after the dimerization. If both 2-nitrophenylthio groups are removed as thiyl radicals, the expected *n*-value is calculated to be 1.5. Therefore, at least one of them must be removed as the sulfenylium ion. Detailed studies on this are now in progress.

Experimental

Materials——*N*-(2-Nitrophenylthio)dibenzylamine (**1**) and six *N*-alkyl-2-nitrobenzenesulfenanilides (**2**—**7**) were prepared from 2-nitrobenzenesulfenyl chloride and the corresponding secondary amines as described previously.[7] *N*-Methylaniline-d_5 was prepared from aniline-d_5 (CEA, France) by the method of Kadin.[8] *N*-Ethylaniline-d_5 was prepared from aniline-d_5 by the method of Nordlander *et al.*[9] **8** and **9** were prepared from the corresponding *N*-alkylaniline-d_5 and purified by chromatography on a pre-packed column, LiChroprep Si 60 (E. Merck, 440-37, size C, 40—60 μm), with benzene–hexane (1 : 1) as an eluent. **8** and **9** were orange-yellow crystals, which had mp's of 82—84.5 and 85—88 °C, respectively. The structures of **8** and **9** were confirmed by the proton and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra.

Methods——ESR spectra were recorded on a JEOL JES-FE 1X spectrometer as described previously.[1] Computer simulation of the spectrum was carried out using a JEOL EC-100 computer system. Proton and ^{13}C-NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard at 400 and 100 MHz, respectively. Cyclic voltammetry was carried out essentially as described previously.[10]

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